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## LABORATORY AUTOMATIC TITRATION OF CHROMIUM PLATING AND ELECTROPOLISHING SOLUTIONS

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# Laboratory Automatic Titration of Chromium Plating And Electropolishing Solutions

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## Abstract

Two increasingly important issues for the metal finishing industry are product quality and productivity. This industry is constantly looking for better methods to monitor key chemical components in its metal finishing solutions. The analytical chemistry literature lacks an adequate automatic titration method for the monitoring of chromic acid in chromium plating solutions and the monitoring of phosphoric and sulfuric acids in electropolishing solutions. Automatic titration methods for each of these applications are given here based on previous manual titration methods. The identical experiment was conducted at three different companies who sell this type of instrument and included calibration, standardization and analysis. Although this work has a specific objective related to chromium plating and electropolishing solutions, the general method is applicable to most other types of metal finishing solution titrations. The optimum operating range of chromic acid in these chromium plating solutions is 240 - 260 g/l while the optimum respective operating ranges of phosphoric and sulfuric acids are 640 - 730 g/l and 795 - 895 g/l. The resulting automatic titration precisions for each application equal the present manual titration precisions from which these methods were derived.

## Keywords

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## Introduction

Two increasingly important issues for the metal finishing industry are product quality and productivity. This industry is constantly looking for better methods to monitor key chemical components in its metal finishing solutions. Titration and specifically automatic titration is a promising technology toward that goal.

Manual titration is an extremely important and proven technique for the quantitative determination of most chemical species. There are many general references on this subject (ref 1-8). Recently it has become possible to adapt many manual titration methods to automated titration methods (ref 9-10). Advantages of automatic titration include reduced operator variability and automatic sampler capability.

The analytical chemistry literature lacks an adequate automatic titration method for the monitoring of chromic acid in chromium plating solutions and the monitoring of phosphoric and sulfuric acids in electropolishing solutions. Lack of optimization of these metal finishing solutions cause serious problems for the chromium plating industry, such as poor quality products, decreased productivity, and wasted resources.

For chromic acid in chromium plating solutions, many manual chemical analysis methods are discussed elsewhere (ref 11). These include hydrometers, atomic absorption spectrometry, inductively coupled plasma spectrometry, manual sodium thiosulfate titration, and manual ferrous ammonium sulfate titration. Only the last two manual methods provide acceptable precision. An automatic titration method is given here based on the last manual method.

For phosphoric and sulfuric acids in electropolishing solutions, many manual chemical analysis methods are discussed elsewhere (ref 12). These include manual sodium hydroxide titration with endpoint detection by indicators, manual sodium hydroxide titration with endpoint detection by first derivative, and manual sodium hydroxide titration with endpoint detection by theoretical endpoint pH values. Only the last two manual methods provide acceptable precision. An automatic titration method is given here based on the last manual method.

## Theory and Background

The analysis of liquids and solids by either manual or automatic titrimetry is one of the most important and useful methods in analytical chemistry. An explanation of this method is necessary for its evaluation as a chemical analysis technique.

Titration methods of analysis are based on measuring the total capacity of an analyte for a reagent. The three general types of titrimetry are volumetric, gravimetric (weight), and

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coulometric titrimetry. In the first and second respective types, the volume or weight of a reagent of known concentration is required to react completely with the analyte determined. In the coulometric type, the "reagent" is a constant direct electrical current of known magnitude that reacts directly or indirectly with the analyte where the quantity measured is the time required for quantitative oxidation or reduction of the analyte (ref 2,8).

The basic types of titrations and measuring systems include precipitation-formation, acid-base, complex-formation, oxidation-reduction, photometric, conductometric, coulometric, polarographic, amperometric and potentiometric methods (ref 1,2,6,8,9,10).

Titration is a quick, accurate, and widely used method for measuring the amount of substance in solution. A standard solution called a titrant is carefully measured by a buret and reacted with an unknown quantity of a second substance. If the volume and concentration of the titrant are known, the unknown quantity of the substance can be calculated. A titration is based on a chemical reaction that may be represented as:

$$aA + bB \longrightarrow products \qquad (1)$$

where A is the titrant, B is the substance titrated, and a and b are the number of moles of each.

The main requirements of a titration are: 1) the reaction must be stoichiometric where a and b are whole numbers; 2) the rate of chemical reaction must be rapid; 3) the reaction must be 99.9% complete and quantitative when a stoichiometric amount of titrant is added; 4) a method must be available for determining the point in the titration at which a stoichiometric amount of titrant has been added and the reaction is complete. Experimental detection of this point by an indicator color change or some change in a electrochemical or physical property of the solution is called the endpoint of the titration. The point at which the theoretical amount of titrant has been added is called the equivalence point of the titration. These two points should coincide but may not for various reasons (ref 2,8).

## Approach

Strict analytical chemistry methods and procedures are followed throughout this experimental section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (ref 2).

Many standard and sample solutions are required. These solutions are prepared or sampled to completely cover the operating ranges of normal production type chromium plating and electropolishing solution concentrations. Two past works by this author (ref 11,12)

provide extensive information for preparing, sampling, and chemically analyzing these solutions for all analytes. These analytical chemistry methods are used for quality control purposes for the solutions.

The general type of analytical system used is the laboratory automatic titrimeter which provides chemical analysis of chromic acid in chromium plating solutions and also phosphoric and sulfuric acids in electropolishing solutions. Identical experiments were conducted on Orion Research's Model 960 Automated Titrimeter System, Mettler Instrument's Model DL70 Automated Titrimeter System, and Brinkmann Instruments' Metrohm Model 670 Automated Titrimeter System. Each company publishes manuals which are an excellent reference for operating conditions and operation and maintenance of these instruments (ref 13-15).

The specifications for each of these systems include an automated titrimeter, pH electrode, platinum redox electrode, automatic sample changer, printer, and computer. Polypropylene and teflon are used throughout these instruments where they come in contact with these acidic sample solutions. The present price of each system is about $15,000.

The experimental approach includes calibration and standardization with standard reference chromium plating and electropolishing solutions followed by analysis with sample chromium plating and electropolishing solutions. Calibration and standardization data were used to determine analyte concentrations of sample solutions.

The experimental method used by each of the three companies for monitoring chromic acid in chromium plating solutions follows.

One analytical reagent grade standard solution is required. This solution is a 4.90 +/- 0.01 g/l potassium dichromate solution that meets American Chemical Society (ACS) Standards and Federal Specification O-C-303D for hexavalent chromium (ref 16-17).

One other reagent grade solution is required. It is a redox titrant which has 45.0 +/ 0.01 grams of ferrous ammonium sulfate (six hydrate) and 60 +/ 1 milliliters of sulfuric acid per liter of total solution.

Preparation of a potassium dichromate standard for redox titration analysis requires that 5 ml of the analytical reagent grade standard solution prepared above is added to the titration vessel. A buret automatically adds 25 ml of deionized water, 1 ml of concentrated sulfuric acid, and 1 ml of concentrated phosphoric acid. Titrate using the redox titrant, platinum electrode, and stirrer to a first derivative endpoint. The endpoint volume is "Reading 1".

Preparation of a chromium plating solution sample for redox titration analysis requires that 10 ml of sample solution is pipeted into a 500 ml volumetric flask which is filled to the mark with deionized water and mixed. Then 5 ml of the diluted sample solution in the flask is added to the titration vessel. A buret automatically adds 25 ml of deionized water, 1 ml of concentrated sulfuric acid, and 1 ml of concentrated phosphoric acid. Titrate using the redox

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titrant, platinum electrode, and stirrer to a first derivative endpoint. This endpoint volume is "Reading 2".

The experimental method used by each of the three companies for monitoring phosphoric and sulfuric acids in electropolishing solutions follows.

Three analytical reagent grade standard solutions are required. The first solution is a 40.00 +/- 0.01 g/l sodium hydroxide solution that is standardized with primary standard potassium acid phthalate (ref 6,18). The second is a 4.00 +/- 0.05 pH unit standard buffer solution and the third is a 10.00 +/- 0.05 pH unit standard buffer solution. These buffer solutions are standardized against primary standard buffer solutions (ref 6).

Preparation of a polishing solution sample for titration analysis requires that 10 ml of sample solution is pipeted into a 250 ml volumetric flask which is filled to the mark with deionized water and mixed. Then pipet 5 ml of the diluted sample solution in the flask into the titration vessel.

Calibration of the pH meter is accomplished using both the pH equals 4.00 and 10.00 buffer solutions. The pH readings for each buffer solution may not vary by more than 0.10 pH units.

Titrate using the sodium hydroxide titrant, pH electrode, and stirrer to both the two first derivative pH endpoints and the two theoretical pH endpoints at 4.50 +/0.10 and 9.70 +/0.10 milliliters. The first and second respective endpoints volumes are "Reading A" and "Reading B" where "Reading B" is the total titrant volume dispensed.

For both sets of experiments, all standard and sample solutions are analyzed in triplicate. Chromic, phosphoric, and sulfuric acid concentrations in the samples are calculated by normal chemical stoichiometry.

## Results and Discussion

Experimental data are presented in Table 1 for the potassium dichromate standard solution and the chromic acid sample solution. The redox titration consists of the following :

$$(Cr_2O_7)^{2-} + 6(Fe)^{2+} + 14(H)+ \longleftrightarrow 2(Cr)^{3+} + 6(Fe)^{3+} + 7(H_2O) \qquad (2)$$
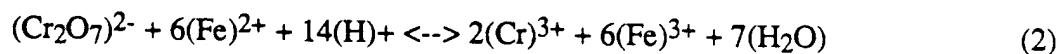
All hexavalent chromium is in the dichromate form due to the addition of sulfuric and phosphoric acids added to the standard and sample solutions above.

Theoretically, from eq. 2, the calculated endpoint of the standard solution requires 21.77 ml of the titrant.

Although all standards and samples are analyzed in their dichromate form, all samples are actually in the chromate form and are reported as chromium trioxide using the following two equations for conversion:

$$(Cr_2O_7)^{2-} + 2(OH)^- <--> 2(CrO_4)^{2-} + H_2O \tag{3}$$

$$(CrO_4)^{2-} + 2(H)^+ <--> CrO_3 + H_2O \tag{4}$$
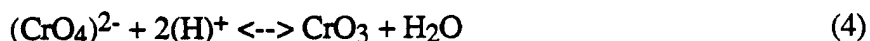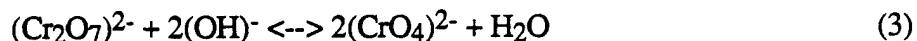
From eq. 3 and eq. 4 it is found that the sodium dichromate standard solution has the equivalent of 245 g/l potassium dichromate or 166.55 g/l chromium trioxide (CrO3).

Therefore, by simple proportion, the calculation for determining the concentration of chromium trioxide in the sample solutions is:
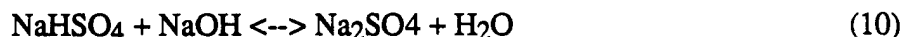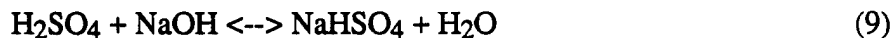
$$g/l \; CrO_3 = (166.55)\frac{Reading \; 2}{Reading \; 1} \tag{5}$$

where Reading 2 is the ml of sample titrant and Reading 1 is the ml of standard titrant.

From eq. 5, the standard and sample solution chromic acid concentrations and related statistics are calculated and given in Table 1 for Benét, Orion, Mettler and Brinkmann.

Previously the variations in precision were evaluated for the materials and methods used (ref 11) and the data is sufficient to adequately monitor these solutions.

Experimental data are presented in Table 2 for the electropolishing solution sample. The acid-base titration consists of the following five equations to various definite extents:

$$H_3PO_4 + NaOH <--> NaH_2PO_4 + H_2O \tag{6}$$

$$NaH_2PO_4 + NaOH <--> Na_2HPO_4 + H_2O \tag{7}$$

$$Na_2HPO_4 + NaOH <--> Na_3PO_4 + H_2O \tag{8}$$

$$H_2SO_4 + NaOH <--> NaHSO_4 + H_2O \tag{9}$$

$$NaHSO_4 + NaOH <--> Na_2SO4 + H_2O \tag{10}$$
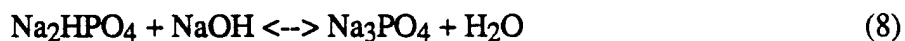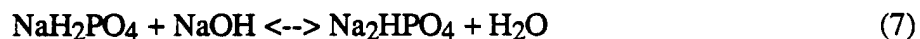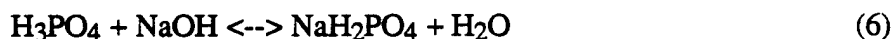
The calculations for determining the concentrations of phosphoric and sulfuric acids in the sample solutions are:

$$g/l \ H_3PO_4 = (B - A)(C)(98)(5) \quad\quad (11)$$

$$g/l \ H_2SO_4 = (2A - B)(C)(49)(5) \quad\quad (12)$$

where A= Reading A, B= Reading B and C= titrant normality. Reading B is the total titrant volume dispensed and the constant values in eq. 11-12 are the combined result of many constants (ref 1,2,6,8).

From eq. 11-12, the sample solution phosphoric and sulfuric acid concentrations and related statistics are calculated and given in Table 2 for Benét, Orion, Mettler and Brinkmann.

Again, the variations in precision were previously evaluated for the materials and methods used (ref 12) and the data is sufficient to adequately monitor the phosphoric and sulfuric acids in these solutions.

Table 3 lists U.S. based automatic titrimeter system sources for sample solutions. As discussed, three manufacturers from this list were chosen for their superior abilities of analyzing chromium plating and electropolishing solutions by this technique.

The optimum operating range of chromic acid in these chromium plating solutions is 240 - 260 g/l while the optimum respective operating ranges of phosphoric and sulfuric acids in these electropolishing solutions are 640 - 730 g/l and 795 - 895 g/l. Both automatic titration methods given here have precisions equal to the present manual titration methods from which they were derived. Although this technique is being used here for chromium plating and electropolishing solution, it is applicable to most chemical species in liquid or solid samples. This includes metal finishing and their associated waste solutions.

Future use of this technology is already under way in two areas. The first area extends the applications given here to include on-stream sampling and dilution before these given automatic titration analyses. Benét is currently working with two other U.S. based sources that have on-stream automatic titrimeter systems. This technology appears promising for chromium plating, electropolishing, and other metal finishing solutions. The second area extends the laboratory and on-stream automatic titration technology to other metal finishing and associated waste solutions. Benét is also currently working in this area.

**Table 1. Titration Of Standard And Sample Solutions Of Chromic Acid In Chromium Plating Solutions**

| | | | Benét | Metrohm | Mettler | Orion |
|---|---|---|---|---|---|---|
| **Exp. Raw Data** | (ml) | | | | | |
| | | standard | | | | |
| | | 1 | 21.45 | 21.15 | 22.13 | 21.95 |
| | | 2 | 21.50 | 21.20 | 22.07 | 21.70 |
| | | 3 | 21.40 | 21.18 | 22.06 | 21.94 |
| | | sample | | | | |
| | | 1 | 31.75 | 31.98 | 32.56 | 32.25 |
| | | 2 | 31.60 | 31.71 | 32.55 | 32.63 |
| | | 3 | 31.50 | 31.98 | 32.46 | 32.50 |
| **Ratio Data*** | | | 1.474 | 1.506 | 1.473 | 1.485 |
| **Conc. Data** | (g/l) | | | | | |
| | | replicate | | | | |
| | | 1 | 246.5 | 251.9 | 245.0 | 244.7 |
| | | 2 | 244.8 | 249.1 | 245.7 | 250.4 |
| | | 3 | 245.2 | 251.5 | 245.1 | 246.8 |
| **Mean** | (g/l) | | 245.5 | 250.8 | 245.3 | 247.3 |
| **Std Dev** | (g/l) | | 0.7 | 1.2 | 0.3 | 2.4 |
| **Rel Std Dev** | (%) | | 0.3 | 0.5 | 0.1 | 1.0 |

Sample volume titrated: Benét used 25 ml; Metrohm, Mettler and Orion used 5 ml.

*This ratio value is the average of the sample volumes divided by the average of the standard volumes.

Note: Orion's programming/calculations are cumbersome.

**Table 2.  Titration Of Sample Solutions Of Phosphoric And Sulfuric Acids In ElectroPolishing Solutions**

| | | | Benét | Metrohm | Mettler | Orion |
|---|---|---|---|---|---|---|
| **Exp Raw Data** * | | | | | | |
| | (ml) | | | | | |
| | | **Reading A** | | | | |
| | | 1 | 24.50 | 24.45 | 24.79 | 24.29 |
| | | 2 | 24.55 | 24.45 | 24.85 | 24.30 |
| | | 3 | 24.50 | 24.44 | 24.85 | 24.32 |
| | | **Reading B** | | | | |
| | | 1 | 31.75 | 31.74 | 32.14 | 31.87 |
| | | 2 | 31.75 | 31.73 | 32.18 | 31.88 |
| | | 3 | 31.75 | 31.75 | 32.16 | 31.85 |
| **$H_3PO_4$ Conc.** | | | | | | |
| | (g/l) | | | | | |
| | | **Replicate** | | | | |
| | | 1 | 710.5 | 714.4 | 719.8 | 742.6 |
| | | 2 | 705.6 | 713.4 | 718.3 | 742.6 |
| | | 3 | 710.5 | 716.4 | 716.4 | 737.9 |
| **Mean** | (g/l) | | 708.9 | 714.7 | 718.2 | 741.0 |
| **Std Dev** | (g/l) | | 2.3 | 1.2 | 1.4 | 2.2 |
| **Rel Std Dev** | (%) | | 0.3 | 0.2 | 0.2 | 0.3 |
| **$H_2SO_4$ Conc.** | | | | | | |
| | (g/l) | | | | | |
| | | **Replicate** | | | | |
| | | 1 | 845.3 | 840.8 | 854.8 | 819.0 |
| | | 2 | 850.2 | 841.3 | 858.2 | 819.4 |
| | | 3 | 845.3 | 839.4 | 859.5 | 822.8 |
| **Mean** | (g/l) | | 846.9 | 840.5 | 857.5 | 820.4 |
| **Std Dev** | (g/l) | | 2.3 | 0.8 | 2.0 | 1.7 |
| **Rel Std Dev** | (%) | | 0.3 | 0.1 | 0.2 | 0.2 |

Sample volume titrated:  Benét used 25 ml; Metrohm and Mettler used 5ml; Orion used 10 ml.

*Both endpoint readings are total volume dispensed in ml.

Note:  Orion's programming/calculations are cumbersome.

### Table 3.  U.S. Automatic Titrimeter Sources For Solutions

Cosa Instrument Corp, Norwood NJ, 201-767-6600
    Mitsubishi (Japan)

Schott/Great Lakes Instr. Inc, Milwaukee WI, 414-355-3601
    Schott/GL (W. Ger.)

Ionics Inc, Watertown MA, 617-926-2500
    Ionics (USA, On-stream only)

\*    Brinkmann, Westbury NY, 516-334-7500
    Metrohm (Swiss)
    Applikon (Holland, On-stream only)

\*    Mettler Instrument Corp, Hightstown NJ, 609-448-3000
    Mettler (Swiss)

\*    Orion Res. Inc, Boston MA, 617-242-3900
    Orion (USA)

Radiometer-America Inc, Westlake OH, 216-871-8900
    Radiometer (USA)

Sanda Inc, Philadelphia PA, 215-849-8100
    Sanda (USA)

Sci. Equip. Co, Aston PA, 215-358-2855
    EM Science (W. Ger.)

\* Experiments were run at these companies

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